MULTI-PHASE CALCIUM SILICATE HYDRATES, METHODS FOR THEIR PREPARATION, AND IMPROVED PAPER AND PIGMENT PRODUCTS PRODUCED THEREWITH

5   ## TECHNICAL FIELD

This invention relates to the manufacturing of novel calcium silicate hydrate ("CSH") crystalline structures, and to pigment products, and novel to paper products produced therewith.

10

BACKGROUND

The paper industry currently utilizes many different types of fillers as a substitute for pulp fiber, as well as to provide desired functional and end-use properties to

15   various paper and paper products. For example, clay has long been used as a filler or fiber substitute. Importantly, the use of clay also provides an improvement in print quality. However, one disadvantage of clay is that it is relatively low in brightness. And, the use of

20   clay in papermaking leads to a decrease in tensile strength of the paper sheet, and to reductions in paper sheet caliper and stiffness.

1

Calcined clay was introduced to the paper industry in an effort to improve brightness and opacity in paper. However, one significant economic limitation of calcined clay is that it is relatively expensive. Also, physically,

5   calcined claim is highly abrasive.

Titanium dioxide, TiO_2, is another example of a filler commonly used in papermaking. Most commonly, titanium dioxide is used to improve opacity of the paper sheet, and, in some cases, it is used to improve sheet brightness as

10   well. Use of titanium dioxide is limited, though, because it is extremely expensive. Unfortunately, it is also the most abrasive pigment on the market today. This is important because highly abrasive pigments are detrimental in the paper industry since they wear down critical paper

15   machine components, such as forming wires, printing press plates, and the like, ultimately leading to high life cycle costs due to the constant repair and maintenance costs.

When calcined clay was first introduced, it was touted as a titanium dioxide extender. Although it did succeed in

20   extending TiO_2, it is nonetheless abrasive, and it is more expensive than either standard clay or market pulp fiber.

2

More recently, and particularly since the mid 1980's, ground calcium carbonate(GCC) has been used as a low cost alkaline filler. Although GCC improved sheet brightness, one downside to GCC was that it too is abrasive. Moreover,

5   use of GCC reduces tensile strength, caliper and stiffness of paper sheets. Consequently, a paper sheet containing GCC tends to be rather limp.

Finally, one of the most commonly used alkaline paper fillers is precipitated calcium carbonate(PCC). PCC is

10   presently one of the best compromise solutions for providing a high brightness filler at an economically feasible price. However, a significant downside to the use of PCC in paper sheets is that PCC provides a lower light scattering power than either TiO_2 or calcined clay. Also,

15   it often reduces sheet strength and stiffness.

Thus, the paper industry still has an unmet need, and continues to look for, a multi-functional pigment that can simultaneously provide two or more of the following attributes:

20   a) cost that are less than TiO_2;

b) better optical properties than calcined clay;

c) better optical properties than GCC;

d) better optical properties than PCC;

3

e) minimal tensile strength loss associated with increased filler usage;

f) at least some improved strength characteristics, such as sheet stiffness.

5

In addition to the just stated criteria, if a paper filler could also simultaneously improve sheet porosity (i.e., provide a more closed sheet) yet provide higher sheet caliper, it would be a very highly desired filler

10 material. To date, no single paper filler with such attributes has been brought to the market. Consequently, the development and commercial availability of such a filler would be extremely desirable.

Finally, the current industry demand for printing

15 papers, especially the rapidly increasing demand for ink jet paper, requires a high performance paper. The performance of such paper would be enhanced by the availability of a pigment that would provide excellent water and oil absorption capacities, so that the paper

20 could quickly capture and prevent ink from spreading or bleeding, as well as aid in surface drying of the ink.

4

Some of the key requirements for an ideal papermaking pigment can be summarized as set forth in Tables 1, 2 and 3 below.

5 Table 1: Idealized Paper Filler Attributes

Sheet Attribute➔	Opacity	Filler Scattering Coefficient	Sheet Scattering Power	Brightness
Industry Requirement ➔	HIGHER than pulp or carbonate fillers	HIGHER than pulp or carbonate fillers	HIGHER than pulp or carbonate fillers	EQUAL OR HIGHER than pulp or carbonate fillers

10

15

Table 2: Key strength parameters for an "Ideal" pigment.

Sheet Attribute	Caliper	Bulk	Porosity	Sheet Smoothness	Stiffness	Tensile
Industry Requirement	HIGHER than pulp sheet alone or with CaCO₃ fillers	HIGHER than pulp sheet alone or with CaCO₃ fillers	HIGHER than pulp sheet alone or with CaCO₃ fillers	HIGHER than pulp sheet alone or with CaCO₃ fillers	HIGHER than pulp sheet alone or with CaCO₃ fillers	HIGHER than pulp sheet alone or with CaCO₃ fillers

Table 3: Key printing requirements for an "Ideal" pigment.

Sheet Attribute	Ink Penetration	Show Through	Print Through
Industry Requirement	LOWER than pulp sheet alone or with CaCO₃ filler	LOWER than pulp sheet alone or with CaCO₃ filler	LOWER than pulp sheet alone or with CaCO₃ filler

Currently, the papermaking industry uses various combinations of available fillers in order to optimize the properties as may be desired in a particular papermaking application. However, because currently available fillers

5   reduce sheet strength to at least some extent, the industry relies on strength additives, such as starch and/or polymers, to maintain the desired paper strength properties when fillers are utilized. Unfortunately, because different pigments have different particle charge

10   characteristics, additions of multiple pigments and additives in the paper making system often create an extremely complicated chemical system which may be somewhat sensitive and difficult to control.

In summary, there remains a significant and as yet

15   unmet need for a high quality, cost effective filler which can be used to simultaneously achieve desired optical properties and sheet strength in paper products. Further, there remains a continuing, unmet need for a method to reliably produce such a pigment which has desirable optical

20   properties and which provides significant cost benefits when compared to the use of titanium dioxide or other pigments currently utilized in the production of paper.

OBJECTS, ADVANTAGES AND NOVEL FEATURES

Accordingly, an important objective of my invention is to provide a process for the manufacture of unique calcium silicate hydrate ("CSH") products, which provide

5   crystalline structures with desired brightness, opacity, and other optical properties.

Another important and related objective is to provide an economical substitute for current paper fillers such as titanium dioxide.

10   A related and important objective is to provide a method for the production of novel paper products using my unique calcium silicate hydrate product.

An important objective is to provide a new calcium silicate hydrate product with low bulk density, good

15   chemical stability (particularly in aqueous solutions), and a high adsorptive capability, among other properties.

These and other advantages, and novel features of my multi-phase calcium silicate hydrates, the method for their preparation, and the improved pigments and paper products

20   produced therewith will become evident and more fully appreciated from full evaluation and consideration of the following detailed description, as well as the accompanying tables and drawing figures.

8

SUMMARY

I have now discovered the process conditions required
to reliably produce unique calcium silicate hydrate
products with particularly advantageous properties for use
5 as a filler in papermaking. The products are produced by
reacting, under hydrothermal conditions, a slurry of burned
lime (quick lime) and a slurry of fluxed calcined
diatomaceous earth (or other appropriate starting siliceous
material). Preferably, a fine slurry of each of the lime
10 and the fluxed silica are utilized.

For one of my CSH products, the lime slurry is
prepared by providing about 1.54 pounds of suspended solids
per gallon of lime slurry. The silica slurry is prepared by
providing about 1.55 pounds of suspended solids per gallon
15 of water. The slaking of the lime slurry raises the
temperature of the slurry to near the boiling point; this
is accomplished before adding the same to the fluxed
silica. The slurry of fluxed calcined diatomaceous earth
is heated to near the boiling point, also, before it is
20 mixed with the lime slurry. When both slurries are near
atmospheric boiling point conditions, then they are mixed
together and stirred, while being retained under pressure
in an autoclave or similar reactor. Temperature of the

9

reaction slurry is raised to between about 245C and 260C, and the reaction is continued for about two hours, more or less. The CaO/SiO2 ratio is maintained, in the feed materials, of about 1.35 (+/- about 0.10) moles CaO to 1

5 mole of SiO2. After the reaction is completed, the product is cooled before the pressure is released and the product crystals are harvested.

Generally, the product of the above described reaction is a multi-phase mixture (i.e., two different forms or

10 phases are present in the product), predominantly of foshagite, with some xonotlite. Importantly, small, haystack like particles containing complex multi-phase crystalline optical fibers are produced that can be advantageously employed in papermaking for coating and for

15 wet end fillers. However, the hydrothermally produced multi-phase crystalline optical fibers are vastly improved over previously produced hydrothermal calcium silicate hydrates of which I am aware, at least with respect to their physical properties, their optical properties, and

20 their utility as a filler in papermaking. Moreover, my unique CSH products are suitable for multiple end uses, such as filler for value added papers, for commodity papers, for newsprint, paper coating applications, as well

as for paints, rubber compositions, and other structural materials.

It is important to appreciate that my hydrothermal process for the manufacture of my unique multiple phase calcium silicate hydrates ("CSH's"), including my novel multi-phase mixture of foshagite and xonotlite, ($CaO_4(SiO_3)(OH)_2$ and $C_6Si_6O_{17}(OH)_2$, respectively), results in a unique mixture of calcium silicate hydrates which have a unique and distinct X-ray diffraction pattern.

Further, the variables that affect the chemical composition of my CSH products, and the primary and secondary structure of the CSH particles and their characteristic properties, can be affected, among other things, by (a) the CaO/SiO_2 mole ratio, by (b) concentration of the CaO and of the SiO_2 in the reaction slurry, (c) the reaction temperature, and (d) the reaction time. By manipulating the just mentioned variables, I have been able to develop two novel pigment products. Those two products can be generally described as follows:

(1) A multi-phase calcium silicate hydrate having a primary phase of foshagite, and a secondary phase of xonotlite. I refer to this product as "TiSil" brand calcium silicate hydrate.

11

(2) A multi-phase calcium silicate hydrate complex

having a primary phase fraction of riversidite with a minor

phase fraction of xonotlite. I refer to this product as

"StiSil" brand calcium silicate hydrate.

5   The first product is formed with a high CaO to SiO_2

mole ratio (about a 1 to 1, to about a 1.7 to 1 ratio of

CaO to SiO2), at a high temperature (~200 °C – 300 °C), with

a low final slurry concentration (~0.4 – 0.6 lb of solids

per gallon of slurry), and with a reaction time of

10   approximately 2 hours. It has a characteristic X-ray

diffraction pattern as shown in Fig. 1. The scanning

electron micrographs (SEMs) of this product are shown in

Figs. 2 and 3. As is evident from the SEMs, this product

consists of primary, fibrous particles joined together, and

15   thus, produces a secondary, three dimensional, "hay-stack"

structure. The physio-chemical characteristics of this

product are unique. For example, extremely high water

absorption is provided. This pigment also provides unique

paper properties when utilized in papermaking. For

20   example, this pigment, when used as a filler, can improve

the optical properties along with sheet strength, sheet

bulk, sheet smoothness, and sheet porosity, simultaneously.

The second product is formed by reacting lime and

silica with a low mole-ratio (about a 0.85 to 1 ratio of

CaO to SiO2), a low reaction temperature (~180 °C to 190

°C), at a high final slurry concentration (~0.7-1.0 pounds

5   of solids per gallon of slurry), and with a reaction time

of approximately 2 hours. This calcium silicate is quite

different from the first product just mentioned above and

its unique X-ray diffraction pattern is given in Fig. 4.

The scanning electron micrographs (SEMs) for this product

10   are given in Figs. 5 and 6. As the SEMs indicate, this

product consists of some fibrous growths that in turn grow

randomly and almost continuously to provide an irregular

globular structure. This product is uniquely formulated to

provide ultra high sheet stiffness when it is used as a

15   filler in paper.

In summary, the unique features of these

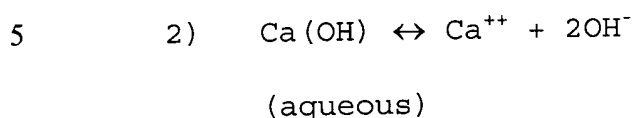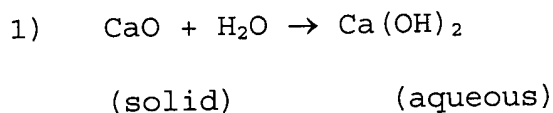hydrothermally produced calcium silicate hydrate products

include:

●   a unique crystallo-chemical composition

20   ●   a multi-phase crystal system

●   a primary and secondary fibrous particle structure

●   a high water absorptivity (in the~300% - 1000% range).

13

The result of the unique properties and physical

structure enable these unique CSH products to provide a

combination of beneficial properties to paper products in a

5   manner heretofore unknown by paper fillers. For example,

the use of these products in paper can increase sheet bulk

and Gurley porosity, simultaneously. In addition, these

products are made up of large particles, but the products

can still scatter light better than PCC, GCC, clay, or even

10   calcined clay.

DETAILED DESCRIPTION

In order to prepare my unique calcium silicate

hydrates (CSH) products, it is first necessary to prepare a

source of calcium. This is normally accomplished by the

5   formation of a slurry of calcious material, most commonly

lime. however, there are several different sources of

calcium, which may be used. Some examples are $CaCO_3$, $CaCl_2$,

and hydrated lime. I have found it advantageous to employ

pebble lime, if less than ½ inch dimension. First, the CaO

10   was slaked in water. The amount and the rate of addition

of lime were set and maintained in order to obtain a

desired concentration of lime slurry. Because the slaking

of lime is an exothermic process, it was necessary to

control both the rate of addition of lime and the quantity

15   of water used. When slaking, the best temperature was

determined to be near boiling, i.e., close to 100 °C (212

°F) in order to form lime particles as fine as possible.

Once the slaking was complete, the lime slurry was then

screened through a 200 mesh screen to remove any grit and

20   oversized particles. The screened and slaked lime slurry

was tested for available lime (as CaO) and then transferred

to an autoclave.

15

The chemistry of the slaking process can be given as

follows:

1) $CaO + H_2O \rightarrow Ca(OH)_2$

(solid)   (aqueous)

5   2) $Ca(OH) \leftrightarrow Ca^{++} + 2OH^-$

(aqueous)

The solubility of calcium hydroxide slurry is

inversely proportional to the temperature, as indicated in

FIG. 7.

10   Next, it is necessary to prepare a slurry of siliceous

material (i.e., a SiO2 slurry). Various siliceous

materials such as quartz, water glass, clay, pure silica,

natural silica (sand), diatomaceous earth, fluxed calcined

diatomaceous earth, or any combination thereof may be

15   utilized as a source of siliceous material. I prefer to

utilize an ultra fine grade of fluxed, calcined

diatomaceous earth. This raw material was prepared into a

slurry of ~1.55 lbs of solids per gallon water. The slurry

was then preheated to near boiling, i.e., near 100 C.

20   Importantly, the solubility of silica (unlike that of

$Ca(OH)_2$), is directly proportional to temperature, as seen

in FIG. 8. For example, quartz (line A in FIG. 8) is only

slightly soluble up to 100 °C. From 100 °C to 130 °C, it

starts solubilizing and around 270 °C, it reaches its

maximum solubility of about 0.07%.

The dissolution of silica can be represented as

follows:

5   3) $(SiO_2)_n + 2n(H_2O) \rightarrow nSi(OH)_4$
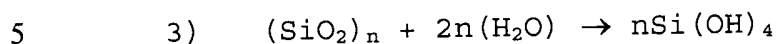
The solubility of silica can be increased by raising

the pH, and/or by using various additives (i.e. sodium

hydroxide). In addition the rate of silica solubility is

10 also a function of particle size, thus to enhance

solubilization of the silica, I prefer to utilize ultra

fine fluxed calcined diatomaceous earth.

Next, the siliceous slurry was mixed with the lime

slurry in an autoclave, to achieve a hydrothermal reaction

15 of the two slurries. Important, the amount of CaO in the

lime slurry and the amount of SiO_2 in the fluxed calcined

diatomaceous earth slurry were pre-selected to provide a

predetermined CaO/SiO_2 mole ratio. Also, the concentration

of the two slurries (CaO and SiO_2) was selected so that the

20 final concentration of the reaction mixture in the

autoclave falls between about 0.2 pounds of solid per

gallon of slurry to about 1.0 pounds of solid per gallon of

slurry.

The hydrothermal reaction itself was carried out in a pressurized vessel, with three major steps:

1) Heating the slurry to the desired temperature (e.g. 180 °C to 300 °C)

2) Reacting at temperature for a specified time (e.g. 60 min to 240 min).

3) Stopping the reaction and cooling down

In my laboratory, the reaction autoclave was cooled by passing quenching water through an internal cooling coil, or by utilizing an external jacketed cooling system. I prefer to utilize a cool down process of from approximately 25 to 30 minutes to drop the temperature from about 230 °C to about 80 °C, as indicated in FIG. 9.

The process steps just mentioned are very important. This is because I have utilized the inverse solubilities of lime and silica with respect to temperature and time in an effort to produce the desired reaction composition, to arrive at the desired multi-phase calcium silicate hydrate product.

Without limiting my invention to any particular theory, I can postulate the following reaction during the hydro-thermal reaction between calcious material and

18

siliceous material. First, during the heating process,

very few free Ca^{++} ions are available. After 100 °C, the

silica starts going into a gel stage. Beyond 130 °C, the

silica ions become available for reacting. As the

5   temperature nears 180 °C, the calcium ion Ca^{++} reacts with

the Si^+ ion to form a metal silicate. The reaction can be

written as follows:

4) $x[Ca^{++} + 2OH^-] + y[Si(OH)_4] \rightarrow CaO_x(SiO_2)_y + (x+y)H_2O$
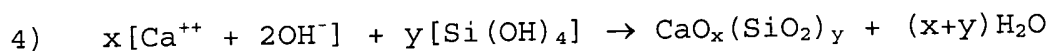
10

Where: x=1 to 6

y=1 to 6

The solid $Ca(OH)_2$ particles react with SiO_2 in the gel

15   phase to give a calcium silicate hydroxide whose crystallo-

chemical structure can be written as $Ca_6Si_6O_{17}(OH)_2$

(Xonotlite). As the temperature is further raised from

180°C to 250 °C, calcium silicate hydride condenses with the

remaining $Ca(OH)_2$ particles to give yet another calcium

20   silicate hydroxide, this time with a distinct X-ray

diffraction pattern and a crystallo-chemical formula of

$CaO_4(SiO_3)_3(OH)_2$ (Foshagite).

19

Further, I have developed my hydrothermal reaction process so that more than one unique calcium silicate hydrate can be produced. In this respect, it is important

5 to note that the following variables are critical in producing a desired end product:

1) Slaking Temperature

2) CaO/SiO_2 mole ratio

10 3) Slurry Concentration

4) Reaction Temperature

5) Reaction Time at Temperature

By changing these variables, a product having several

15 different phases of calcium silicate hydroxide can be produced. Some of these phases may include:

		X-ray Diffraction peaks	
Formula	Morphology	Major	Minor
$Ca_4(SiO_3)_3(OH)_2$	Foshagite	d=2.93 Å,	d=2.16 Å, d=4.96 Å
$Ca_6Si_6O_{17}$	Xonotlite	d=3.02 Å,	d=2.04 Å , d=8.50 Å
$Ca_5Si_6O_{17}(OH)_2$	Riversideite	d=3.055 Å,	d=3.58 Å , d=2.80 Å

20

Although not normally important, one should note that my final product CSH composition may also contain minor amounts of calcite - aragonite, produced as a result of side reactions.

5   The first and most important product of my process is a multi-phase CSH composition having various amounts of phases of matter represented by $CaO_4(SiO_3)_3(OH)_2$ (Foshagite) and $Ca_6Si_6O_{17}(OH)_2$ (Xonotlite). A unique X-ray diffraction pattern for this product is provided in FIG. 1. In that

10   XRD, the crystallochemical formula of the mixture, and the characteristic d spacings, are given below:

(Phase I)   (Major)

Foshagite $CaO_4(SiO_3)_3(OH)_2$ d=2.97Å, d=2.31Å, d=5.05Å

15   (Phase II)   (Minor)

Xonotlite $Ca_6Si_6O_{17}(OH)_2$ d=3.107Å, d=1.75Å, d=3.66Å

The Scanning Electron Micrographs (SEMs) representing this first product are provided in FIG. 2 and 3. As shown

20   in FIG. 2 and 3, it is important to note that the product consists of primary particles and secondary particles. The primary particles have a diameter between 0.1 and 0.2 microns and a length between 1.0 and 4.0 microns. FIG. 3

also indicates that the primary particle has two phases. The rod or ribbon like structure is characteristic of xonotlite ($Ca_6Si_6O_{17}(OH_2)$) while the predominant structures are thin and fibrous, characteristic of foshagite

5 ($Ca_4(SiO_3)_3(OH)_2$). The diameter of the foshagite crystals ranges from 0.1 to 0.3 microns and the length is ranges from 2.0 to 5.0 microns.

The SEM of FIG. 3 reveals a secondary, three dimensional structure. This three dimensional structure is

10 believed to be formed by the interlocking of the fibrous material and the continuous growth of the "gel" like material at the intersection of the individual particles. This may also be the reason that the secondary structure is fairly stable. Importantly, the secondary structure can

15 generally withstand the shear forces encountered during the discharge of material from pressure vessels after the reaction has completed, as well as shear forces encountered during papermaking. This is seen, for example, in that the secondary structure maintains its "bulk density" during

20 some of the end use processes such as calendering during paper making. The particle size of secondary structure, as measured by particle size measuring devices like the Malvern Mastersizer, is in the range of 10-40 microns.

The calcium silicate hydroxide mixture of my invention also has very high brightness characteristics. A comparison with other pigments is given below:

Various pigments and their typical published
5   brightness values are as follows:

Pigment	GE (TAPPI) Brightness (%)
Calcium Silicate Hydrate (TiSil Brand CSH)	95-97
Calcined (High Brightness) Clay	89-91
Filler Clay	85-88
Synthetic Silica	97-100
Calcium Carbonate	95 ± 1

One of the most significant characteristics of the composition of matter produced by my process is the ability of these multiple phase calcium silicates to absorb large
10   amounts of water. These calcium silicates can adsorb anywhere from 350% to 1000% of their weight. This high water absorption capacity makes my pigment extremely well suited for preventing ink strike through in writing and printing papers, newsprint and more.

15

Example 1: Manufacture of multiple phase silicate hydrates
(5XPC 12)

Initially, 135.09 grams of 1/2" rotary pebble lime
(Mississippi Lime Co.) was accurately weighed and slaked in
5   410 milliliters of de-ionized water. The slaking reaction
is exothermic and caused the slurry temperature to rise to
near boiling. When the slurry temperature was very near
boiling and before much of the water had evaporated, an
additional 1190 milliliters of water was added to both
10 dilute and cool the slurry. The slurry was then agitated
for 30 minutes to insure slaking completion before being
screened through a 140 mesh screen. The slurry was then
transferred to 5 liter autoclave and tested for lime
availability in accordance with ASTM method C25. The
15 autoclave is fitted with an outside heating element
contained in an insulated jacket housing. The autoclave is
also fitted with a variable speed magnetic drive for
stirring the slurry during reaction. Approximately 109.6
grams of ultra fine fluxed calcined diatomaceous earth was
20 weighed and added to 750ml of hot water (concentration of
~1.22lb/gallon). The silica slurry was heated for
approximately 10min, to near boiling, then added to the
screened and tested lime slurry. The exact amount of

24

silica slurry added to lime slurry was determined by the

lime availability such that a mol ratio of 1.35 mol CaO/SiO_2

would be maintained. The total slurry volume was also

adjusted to a final concentration of 0.425 lb/gallon. The

5   high pressure vessel was then closed, sealed, and connected

to an automated heating/cooling control system (RX 330).

The contents of the autoclave were under constant agitation

via the magnetic drive motor mentioned above.

The high pressure reactor was heated by an externally

10   jacketed heating element. The autoclave was continuously

agitated at a constant speed of 338rpm. The reactor was

heated for approximately 100 min in order to reach the

target temperature of 245 °C (473 °F). The temperature was

maintained at 245 °C for 2 hours, after heating to the

15   target temperature was accomplished, with the use of the

heating/cooling controller. At the end of the reaction,

the "quenching" water was flushed through the cooling coil

built inside the autoclave. This cooling process was

maintained until the inside vessel temperature reached

20   approximately 80 °C(approximately 30min). At which point,

the vessel was opened and the reaction products were

transferred to a holding vessel for storage. A portion of

the resultant slurry was dried in a 105 °C oven for 12

25

hours. During the drying process, the slurry formed hard
lumps, which had to be broken up through the use of a
mortar and pestle. The now powdered, dry product was
brushed through a 140 mesh screen to insure product

5   uniformity when testing. The pigment in this example was
designated 5XPC 12. The test carried out on the dry powder
were as follows:

1)   X-ray diffraction analysis

10   2)   Scanning Electron Micrograph (S.E.M.)

3)   Brightness

4)   Percent Water Absorption

5)   Air Permeability (Blaine Method)

6)   pH

15

For the air permeability test, two numbers are
reported. The first is the weight in grams of powder
required to fill the capsule and is an indication of the
"bulk density" of the powder. The second is the time in

20   seconds for a controlled volume of air to pass through the
compressed powder inside the capsule and is an approximate
measure of the "structure" of the particle.

The process conditions are given in Table 1a and the pigment properties are given in Table 1b.

Table 1a: Process conditions of 5XPC 12

Batch #	Mol Ratio (CaO/SiO$_2$)	Concentration (lb/gallon)	Temperature (°C)	Average Pressure (psi)	Reaction Time (hours)
5XPC 12	1.35	0.425	245	456	2.0

5

Table 1b: Pigment Properties of 5XPC 12

Batch #	GE Brightness (% reflectance)	Water Absorption (%)	Air Permeability Blaine Wt. (g)	Air Permeability Blaine time (sec.)
5XPC 12	96.4	880	0.35	81.8

The x-ray diffraction pattern of this novel,

multiphase calcium silicate hydrate is given in FIG. 1.

This product (identified as 5XPC 12) gave a unique x-ray

pattern. The pattern indicated that the powder had one

5   major phase and one minor phase. The summary of the

characteristic "peaks" is shown in Table 1c.

The major peaks for phase I were found to indicate the

presence of calcium silicate hydroxide - Foshagite -

10 $(Ca_4(SiO_3)_3(OH)_2)$ with major peaks at $d(Å)=2.97$, $d(Å)=2.31$

and a minor peak at $d(Å)=5.05$. For phase II, the x-ray

diffraction pattern indicated the presence of calcium

silicate hydrate - Xonotlite - $(Ca_6Si_6O_{17}(OH)_2)$ with major

peaks at $d(Å)=3.107$, $d(Å)=1.75$ and a minor peak at

15 $d(Å)=3.66$. Thus I obtained a novel combination of

Foshagite and Xonotlite from a single reaction.

Table 1c: X-ray diffraction peak summary for 5XPC 12

Common Name	Crystallochemical Formula	d-spacing (Major)	d-spacing (median)	d-spacing (Minor)
Foshagite (Phase I)	$CaO_4(SiO_3)_3(OH)_2$ (Major)	d=2.97Å	d=2.31Å	d=5.05Å
Xonotlite (Phase II)	$Ca_6Si_6O_{17}(OH)_2$ (Minor)	d=3.107Å	d=1.75Å	d=3.66Å

The S.E.M. pictures at 10,000 times and 2000 times magnification are given in FIG. 2 and 3, respectively. The high magnification S.E.M. clearly shows the fibrous structure of Foshagite and a small fraction of "rod" or

5   "ribbon" like, tubular structures of Xonotlite.. The diameter of the Foshagite "fibers" ranges from 0.1 to 0.2 microns while the length ranges from 1 to 5 microns. The Xonotlite particles had diameters in the range of 0.1 to 0.3 microns and a length in the range of 1 to 3 microns.

10   The low magnification S.E.M. depicts the three dimensional structure of the secondary particles of calcium silicate hydrates. The structure appears to have been formed by an interlocking of the primary "fibrous" crystals and some inter-fiber bonding due to hydrogel of silica

15   formed during the initial stages of hydro-thermal reaction. Because of these two main reasons, the secondary particles are fairly stable and do not significantly lose their 3-d structure when subjected to process shear. In addition, these particles also seem to withstand the pressure

20   encountered during the calendering or finishing operations integral to papermaking. The median size of the secondary particles as seen, ranges from 10 to about 40 microns.

In order to evaluate this pigment in paper, handsheets were prepared for evaluation. Handsheets were prepared using the 5XPC 12 product sample in order to evaluate the papermaking characteristics of the pigment. The procedure

5   included preparation of a standard pulp slurry made up of 75% hardwood and 25% softwood. Both pulp sources were beaten separately, in a Valley Beater, to a specific Canadian Standard Freeness of 450 ± 10 in accordance with TAPPI test methods T-200 and T-227. Handsheets were formed

10 from the prepared stock, on a 6" British handsheet mold, in accordance with TAPPI test method T-205. The exceptions to the standard method were as follows. Since the goal of producing these handsheets was to test filler performance, some filler was incorporated into the handsheets at various

15 replacement levels (usually 15%, 20%, and 25%). In order to achieve comparability between different levels, a constant basis weight was achieved via a reduction in fiber content. Thus, a 25% filled sheet would contain only 75% of the fiber that the unfilled sheet had. The next

20 variation on the standard test method was the addition of retention aid. A retention aid (Percol 175) was added to hold the filler in the sheet until the sheet had dried

30

completely. All other handsheet formation components were kept consistent with TAPPI test method T-205.

The handsheets were tested in accordance with TAPPI test method T-220, with one exception. Instead of using a 15mm sample for testing tensile, a 25.4mm sample was used and the tensile index calculations were altered accordingly. The handsheets were ashed in accordance with TAPPI test method T-211.

Paper handsheets were tested for the following properties:

1. Opacity

2. Sheet Scattering Coefficient

3. Filler Scattering Coefficient

4. Brightness

5. Sheet Bulk (Basis Weight/Caliper ratio)

6. Sheet Stiffness

7. Sheet Porosity

8. Sheet Smoothness

9. Sheet Tensile Index

A standard alkaline filler, precipitated calcium carbonate (SMI Albacar HO), was used as a reference material to gauge product performance. The results of the handsheet evaluation are given in Tables 1d and 1e.

31

Table 1d: Optical property performance of handsheets

containing 20% (interpolated) 5XPC 12 and pulp only.

Pigment	Brightness (ISO)	Opacity (ISO)	Sheet Scattering Coefficien t (cm^2/g)	Filler Scattering Coefficien t (cm^2/g)
5XPC 12	90.56	90.88	835.21	3077.24
Pulp Only	85.73	73.19	274.8	NM
Improvement over pulp	+ 5.6%	+ 24.2%	+ 203.9%	-

5   Table 1e: Strength property performance of handsheets

containing 20% (interpolated) 5XPC 12 and pulp only.

Pigment	Stiffness (Gurley Units)	Bulk (cm^3/g)	Porosity (sec/100cc air)
5XPC 12	150.74	1.73	64.91
Pulp Only	137.15	1.40	51.94
Improvement over pulp	+ 9.9%	+ 23.3%	+ 25.0%

10

Table 1f: Optical property performance of handsheets containing 20% (interpolated) 5XPC 12 and 20% (interpolated) PCC.

Pigment	Brightness (ISO)	Opacity (ISO)	Sheet Scattering Coefficient (cm^2/g)	Filler Scattering Coefficient (cm^2/g)
5XPC 12	90.56	90.88	835.12	3077.24
PCC	90.44	88.69	709.84	2474.48
Improvement over PCC	Even	+ 2.47%	+ 17.66%	+ 24.36%

5   Table 1g: Strength property performance of handsheets containing 20% (interpolated) of 5XPC 12 and 20% (interpolated) PCC.

Pigment	Bulk (cm^3/g)	Porosity (sec/100cc air)	Stiffness (Gurley Units)	Tensile Index (Nm/g)
5XPC 12	1.73	64.91	150.74	31.17
PCC	1.55	22.24	107.54	27.95
Improvement over PCC	+ 11.56%	+ 191.9%	+ 40.17%	+ 11.53%

33

Example 2 - (5XPC - 27 pigment sample)

This novel, multiphase calcium silicate hydrate was
formed by hydro-thermal reaction of lime and silica. The

5   CaO/SiO_2 mol ratio used for this new product was 0.85, the
final slurry concentration was ~0.8 lb/gallon, the reaction
temperature was 190 °C, and the reaction time was 2.5 hours.
A summary of these conditions is given in Table 2a.

A totally new product was formed using a new set of

10 reaction conditions. First, the CaO/SiO_2 mol ratio was
adjusted to 0.85, the reaction temperature was set to 190
°C, the slurry concentration was increased to 0.75
lbs/gallon, and the reaction time was increased to 2.5
hours. The product of this example was designated 5XPC 27.

15 A summary of the reaction conditions is given in Table 2a.

Table 2a: Process conditions of 5XPC 27

Batch #	Mol Ratio (CaO/SiO_2)	Concentration (lb/gallon)	Temperature (°C)	Average Pressure (psi)	Reaction Time (hours)
5XPC 27	0.85	0.75	190	163.5	2.5

34

The resulting calcium silicate hydrate was tested for pigment brightness, water absorption, Blaine air permeability and density, and pH. Both X-ray diffraction and Scanning Electron Micrograph analyses were also

5   performed on this product. The pigment properties are given in Table 2b. The pigment was evaluated for its performance in paper by incorporating it into handsheets as in example 1. The results of the handsheet work are given in Tables 2d and 2e. The X-ray diffraction pattern is

10   given in FIG. 4. The S.E.M. pictures at 10,000 and 2000 times magnification are given in FIG. 5 and 6, respectively.

The calcium silicate hydride formed under these conditions had substantially lower brightness and water

15   absorption characteristics than TiSil Brand CSH set forth in Example 1. However, it gave much higher sheet bulk and sheet permeability characteristics. The pigment properties of my novel 5XPC 27 pigment are given in Table 2b. It appears that this product provided a much higher sheet

20   bulk. Also, the sheet permeability of this new product was higher than the Foshagite-Xonotlite complex as described in Example 1.

Table 2b: Pigment Properties of 5XPC 27

Batch #	G.E. Brightness (% reflectance)	Water Absorption (%)	Air Permeability Blaine Wt. (g)	Air Permeability Blaine time (sec.)
5XPC 27	91.2	360	0.5	17.0

As the mole ratio of CaO/SiO_2 was reduced to ~0.85 and the reaction temperature was lowered to 190 °C, I discovered

5   another unique and useful multiple phase calcium silicate hydrate material with a distinct and unique X-ray diffraction pattern. The X-ray diffraction analysis revealed this product to be a mixture of Riversidite $[Ca_5Si_6O_{16}(OH)_2]$ and Xonotlite $[Ca_6Si_6O_{17}(OH)_2]$. The X-ray

10   diffraction pattern is given in Fig. 4. The pattern indicated that the powder had one major phase and one minor phase. The peak summary is shown in Table 2c.

15

36

Table 2c: X-ray diffraction peak summary for 5XPC 27

Common Name	Crystallochemical Formula	d-spacing (Major)	d-spacing (Median)	d-spacing (Minor)
Riversideite (Phase I)	$Ca_5Si_6O_{16}(OH)_2$ (Major)	d=3.055Å	d=3.58Å	d=2.80Å
Xonotlite (Phase II)	$Ca_6Si_6O_{17}(OH)_2$ (Minor)	d=3.056Å	d=4.09Å	d=2.50Å

The major peaks for phase I were found to indicate the

presence of calcium silicate hydrate - Riversideite -

5    $(Ca_5Si_6O_{16}(OH)_2)$ with major peaks at $d(Å) = 3.055$, $d(Å) = 3.58$

and a minor peak at $d(Å) = 2.80$. For phase II, the pattern

indicated the presence of calcium silicate hydroxide -

Xonotlite - $(Ca_6Si_6O_{17}(OH)_2)$ with major peaks at $d(Å) = 3.056$,

$d(Å) = 4.09$ and a minor peak at $d(Å) = 2.50$. The pigment

10   also contained trace amounts of calcite $(CaCO_3)$. The other

portion of the slurry was tested for the pigment

performance as a filler in paper. The paper was formed

into handsheets and tested using the procedures described

in example 1.

15   The S.E.M. pictures at 10,000 times and 2000 times are

given in Figs. 5 and 6. As can be seen in the 10,000x

magnification photograph, the product is unlike the

previous example. The calcium silicate hydrate mixture has

fibrous and non-fibrous composition joined possibly by an

37

amorphous portion of silica hydrogel formed during the initial phase of hydro-thermal reaction.

The 2000x magnification indicates the formation of an irregular globular particle formed by the fibrous inter-growth of a series of primary fibrous crystals. The particle size is in the range of 10-30 microns and the crystals seem to have grown randomly.

This multi-phase (primarily Riversideite and Xonotlite) calcium silicate hydrate gave lower brightness value than that of Example 1. More significantly, this material gave a much lower water absorption (around 360% - 400%) as well.

To evaluate performance in paper, handsheets were formed using this pigment and then tested as in Example 1. The paper performance results are shown in Tables 2d-g.

This product, compared to pulp only, gave substantially higher stiffness and sheet bulk. Unlike the pigment provided in Example 1, (where Foshagite was the primary component), this second pigment (where Riversideite and Xonotlite are present) combination produced a much more open sheet, as shown by the low Gurley porosity numbers. The optical properties, like brightness, opacity and scattering coefficient of the sheet decreased.

38

Comparing the performance of this second pigment (with predominantly Riversidite and Xonotlite present) with an alkaline filler, such as precipitated calcium carbonate, the sheet stiffness and bulk improved dramatically. The optical properties (sheet opacity, sheet brightness, etc.)of the handsheets decreased, however. The decreased optical properties of this new multiphase product, were clearly due to the large particle size and irregular globular structure as seen in the S.E.M. pictures.

Table 2d: Optical property performance of handsheets containing 20% (interpolated) 5XPC 27 and pulp only.

Pigment	Brightness (ISO)	Opacity (ISO)	Sheet Scattering Coefficient (cm^2/g)	Filler Scattering Coefficient (cm^2/g)
5XPC 27	87.86	83.35	449.12	1092.42
Pulp Only	85.19	74.97	292.1	N/A
Improvement over pulp	+ 3.1%	+ 11.2%	+ 53.8%	-

Table 2e: Strength property performance of handsheets containing 20% (interpolated) 5XPC 27 and pulp only.

Pigment	Stiffness (Gurley Units)	Bulk (cm³/g)	Porosity (sec/100cc air)
5XPC 27	225.87	2.46	3.92
Pulp Only	136.68	1.47	33.5
Improvement over pulp	+ 65.2%	+ 68.0%	- 88.3%

Table 2f: Optical property performance of handsheets containing 20% (interpolated) 5XPC 27 and 20% (interpolated) PCC.

Pigment	Brightness (ISO)	Opacity (ISO)	Sheet Scattering Coefficient (cm²/g)	Filler Scattering Coefficient (cm²/g)
5XPC 27	87.86	83.35	449.12	1092.42
PCC	90.21	89.39	738.55	2546.03
Improvement over PCC	2.6%	- 6.76%	- 39.19%	- 57.09%

Table 2g: Strength property performance of handsheets

containing 20% (interpolated) of 5XPC 27 and 20%

(interpolated) PCC.

Pigment	Stiffness (Gurley Units)	Bulk (cm³/g)	Porosity (sec/100cc air)	Tensile Index (Nm/g)
5XPC 27	225.87	2.46	3.92	29.67
PCC	102.11	1.65	13.23	24.77
Improvement over PCC	+ 121.19%	+ 49.22%	- 70.39%	+ 19.79%

5   Thus, this multiphase combination of calcium silicate

hydrate was most useful in improving sheet stiffness and

sheet bulk. It was also excellent for "opening up" the

sheet (lowering the Gurley porosity) for more "breathing."

Due to its excellent stiffness, I refer to this product as

10   "StiSil Brand CSH."

Example 3: Varying Reaction Temperature (XPC 119)

Initially, 39.9 grams of pebble lime was weighed

accurately and added slowly to 1.2L of water in a beaker

15   with constant agitation. The amount of lime , water, and

the rate of lime addition were controlled in an effort to

keep the slurry from boiling due to the exothermic nature of the lime slaking reaction. The slaked lime of $Ca(OH)_2$ was screened in a 200 mesh screen. The residual material was then discarded. The filtered $Ca(OH)_2$ slurry was tested

5 by acidic titration to calculate the exact amount of available lime. The slaked lime was then transferred into a 2 liter autoclave. Then, 31.06 grams of ultrafine, calcined diatomaceous earth was added to 200 ml of water in order to produce a slurry of 0.1553 g/L concentration.

10 This slurry was also preheated with constant stirring and brought to near boiling (near 100 °C). Next, the silica was added to the autoclave containing the hot slaked lime slurry. The total solids concentration of the $CaO + SiO_2$ slurry inside the autoclave, at this point was ~0.5

15 lbs/gallon. The mol ratio of lime to silica was 1.67 CaO/SiO_2. The high-pressure reactor was sealed and then heated by an externally, jacketed, electrical heating element.

The autoclave was simultaneously agitated at a

20 constant speed magnetic drive motor at 600 RPM. The autoclave was heated until a preset temperature of 220 °C was reached. At that point the reaction conditions were held constant by a system controller, RX-32. The $CaO + SiO_2$

42

slurry was reacted at a temperature of 220 °C for 120

minutes. At the end of this time, the "quenching" water

was passed through a cooling system built into the inside

of the autoclave. Inside the pressure vessel, steam

5   condensed and the temperature fell rapidly. The cooling

water continued until the vessel reached approximately 80

°C.

The silicate slurry was transferred into a holding

beaker. The following describes the overall heating /

10   cooling cycle (see Fig. 5):

-       Time to temperature ~ 100 min

-       Time at temperature ~ 120 min

-       Time for cooling ~ 25 min

15   A portion of the slurry was tested for the following

properties:

1)   X-Ray Diffraction Analysis

2)   Scanning Electron Microscope (S.E.M)

3)   Brightness

20   4)   Water Absorption

5)   Blaine Air Permeability (ASTM/ASTM C204-78a)

• Sample Weight (g) - Indication of Bulk Density

• Time (in sec) for a fixed volume of air to pass
  through the volume of sample - Indication of
  particle packing or structure

5   The reaction conditions and pigment properties are
given in Tables 3a and 3b respectively.

Example 4: Varying Reaction Temperature (XPC 107)

In this example, all the reaction conditions and
10   parameters were identical to example 3 above, except for
the reaction temperature was raised from 220 °C to 233 °C.
The resultant calcium silicate hydrate complex was then
tested as per the above-described test program and the
resultant reaction conditions and pigment properties are
15   given in Tables 3a and 3b respectively.

Example 5: Varying Reaction Temperature (XPC 124)

In this example, all of the reaction conditions and
parameters were kept constant, as in example 3, except for
20   reaction temperature. The reaction temperature was raised
from 233 °C to 243 °C. The calcium silicate hydrate complex
formed was tested as in the above examples. The reaction

conditions and pigment properties are given in Tables 3a

and 3b respectively.

Table 3a: Reaction conditions for Examples 3, 4, and 5.

Example #	Batch ID	Mole Ratio (CaO/SiO$_2$)	Conc. (lbs/gal)	Temp (degrees C)	Reaction Time (hours)
Example 3	XPC 119	1.67	0.7	220.0	2
Example 4	XPC 107	1.67	0.7	233.0	2
Example 5	XPC 124	1.67	0.7	243.0	2

5

Table 3b: Pigment properties for Examples 3, 4, and 5.

Example #	Water Absorption (%)	Brightness (ISO)	Blaine Wt. (grams)	Blaine Time (sec.)	pH
Example 3	440	94.2	0.5	94	11.6
Example 4	440	96.2	0.45	118.5	10.7
Example 5	580	94.9	0.35	94.9	11.5

Note that the mid range reaction temperature of 233 °C

produced the highest brightness material

10

Example 6: Varying the CaO/SiO$_2$ mol ratio (XPC 130)

In this example, all the reaction parameters were kept

constant, as in example 4, except for the CaO/SiO$_2$ mol

ratio. The CaO/SiO$_2$ mol ratio was changed to 1.4.

15   Then, 69.0g of SiO$_2$ and 78.0g of CaO were mixed to give

a CaO/SiO$_2$ mol ratio of 1.4. The two slurries, CaO and SiO$_2$

were mixed in the autoclave. The concentration in the

45

autoclave was adjusted by adding water to 0.7 lb/gal. The

reaction was carried out for two hours and the autoclave

was cooled and the product was handled as in example 1.

The reaction temperature was kept constant at 233 °C. The

5   reaction mixture was agitated at a constant speed via a

magnetic drive motor attached to the autoclave. The motor

was rotated at 600 RPM. The final product was tested for

key parameters and the reaction conditions and key pigment

properties are shown in Tables 4a and 4b respectively.

10

Example 7: Varying the CaO/SiO$_2$ mol ratio (XPC 132)

In this example, all the reaction parameters were kept

constant as in example 4, except the CaO/SiO$_2$ mol ratio was

raised to 1.6. The hydrothermal reaction was carried out

15   using the same cycle of heating and cooling as in the

previous examples and the final product was again tested

for key pigment properties. The reaction conditions and

key pigment properties are shown in Tables 4a and 4b

respectively.

20

Example 8: Varying CaO/SiO$_2$ mol ratio (XPC 134)

Here again, the reaction parameters were all held

constant, as in example 4, except for the CaO/SiO$_2$ mol

46

ratio, which was raised to 1.8. The hydrothermal reaction was carried out using the same cycle of heating and cooling as in the previous examples and the final product was again tested for key pigment properties. The reaction conditions

5 and key pigment properties are shown in Tables 4a and 4b respectively.

Table 4a: Reaction conditions for Examples 6, 7, and 8.

Example #	Batch #	Mole Ratio (CaO/SiO_2)	Conc. (lbs/gal)	Temp. (degrees C)	Reaction Time (hours)
Example 6	XPC 130	1.4	0.7	233.0	2
Example 7	XPC 132	1.6	0.7	233.0	2
Example 8	XPC 134	1.8	0.7	233.0	2

10 Table 4b: Pigment properties for Examples 6, 7, 8.

Example #	Water Absorption (%)	Brightness (ISO)	Blaine Wt. (grams)	Blaine Time (sec.)	pH
Example 6	380	94.7	0.45	112	10.9
Example 7	420	94.1	0.45	51.9	11.4
Example 8	400	94.7	0.5	57.8	11.7

Note that a CaO/SiO_2 mole ratio of 1.6 produced a calcium silicate hydrate with the highest water absorption capability.

15

47

Example 9: Varying Reaction Time (XPC 172)

In this example, all the process conditions were kept constant, as in example 7, except for the reaction time, which was lowered to 1 hour. The calcium silicate hydrate

5   complex was tested as in the previous examples and the reaction conditions and key pigment properties are shown in Tables 5a and 5b respectively.

Example 10: Varying Reaction Time (XPC 173)

10   In this example, all the process conditions were kept constant, as in example 9, except for the reaction time, which was raised to 2 hours. The calcium silicate hydrate complex was tested as in the previous examples and the reaction conditions and key pigment properties are shown in

15   Tables 5a and 5b respectively.

Example 11: Varying Reaction Time (XPC174)

In this example, all the process conditions were kept constant, as in example 9, except for the reaction time,

20   which was raised to 3 hours. The calcium silicate hydrate complex was tested as in the previous examples and the reaction conditions and key pigment properties are shown in Tables 5a and 5b respectively.

48

Table 5a: Reaction conditions for Examples 9, 10, and 11.

Example #	Batch #	Mole Ratio (CaO/SiO$_2$)	Conc. (lbs/gal)	Temp. (degrees C)	Reaction Time (hours)
Example 9	XPC 172	1.67	0.7	233.0	1
Example 10	XPC 173	1.67	0.7	233.0	2
Example 11	XPC 174	1.67	0.7	233.0	3

Table 5b: Pigment properties for Examples 9, 10 and 11.

Example #	Water Absorption (%)	Brightness (ISO)	Blaine Wt. (grams)	Blaine Time (sec.)	PH
Example 9	480	92.9	0.5	74	11.1
Example 10	520	96.1	0.45	108.5	11.0
Example 11	600	93.3	0.4	135.0	11.2

Note that a reaction time of 2 hours produced the highest brightness product. The longer reaction time of 3 hours produced the greatest water absorption values, but at a lower brightness.

Example 12: Varying CaO-SiO$_2$ Slurry Concentration (XPC 136)

In this example, all the reaction conditions were kept constant, as in Example 7, except for the CaO/SiO$_2$ slurry concentration, which was lowered to 0.4 lb/gallon. To start, 49.6 g of lime was slaked, screened, and titrated

49

for available CaO. Then, 34.2g of ultra-fine fluxed

calcined diatomaceous earth was slurried. The fluxed

calcined diatomaceous earth slurry was added to the lime

slurry to give the mixture an initial CaO/SiO_2 mol ratio of

5   1.6. The reactants were then placed in a 2.0 liter

autoclave and water was added to bring the final

concentration of $CaO+SiO_2$ slurry up to 0.4 lb/gallon. The

reaction temperature was set at 233 °C. The autoclave was

set and controlled using a temperature controller for both

10   heating and cooling cycles as shown in Fig. 9. The silica-

lime slurry was reacted at 233 °C for two hours. At the end

of the reaction, the resulting calcium silicate hydrate was

cooled by circulating water through the jacketed autoclave.

The resulting mass was transferred to a holding beaker.

15   The product was tested for the same key parameters and with

the same methods as described in example 3. The reaction

conditions and key pigment properties are shown in Tables

6a and 6b, respectively.

20   Example 13 Varying CaO - SiO_2 Slurry Concentration (XPC 138)

In this reaction, all the reaction parameters were

kept constant, as in example 12, except for the CaO + SiO_2

slurry concentration, which was raised to 0.6 lb/gallon.

50

The product was tested as in Example 3 and the reaction conditions and key pigment properties are shown in Tables 6a and 6b, respectively.

5   Example 14 Varying CaO - SiO_2 Slurry Concentration (XPC 140)

In this reaction, all the reaction parameters were kept constant, as in example 12, except for the CaO + SiO_2 slurry concentration, which was raised to 0.8 lb/gallon. The product was tested as in example 3 and the reaction

10   conditions and key pigment properties are shown in Tables 6a and 6b, respectively.

Example 15 Varying CaO - SiO_2 Slurry Concentration (XPC 141)

In this reaction, all the reaction parameters were

15   kept constant, as in example 12, except for the CaO/SiO_2 slurry concentration, which was raised to 0.9 lb/gallon. The product was tested as in example 3 and the reaction conditions and key pigment properties are shown in Tables 6a and 6b, respectively.

20

Table 6a: Reaction conditions for Examples 12, 13, 14, 15.

Example #	Batch #	Mole Ratio (CaO/SiO$_2$)	Conc. (lbs/gal)	Temp. (degrees C)	Reaction Time (hours)
Example 12	XPC 136	1.6	0.4	233	2
Example 13	XPC 138	1.6	0.6	233	2
Example 14	XPC 140	1.6	0.8	233	2
Example 15	XPC 141	1.6	0.9	233	2

Table 6b: Pigment properties for Examples 12, 13, 14, 15.

Example #	Water Absorption (%)	Brightness (ISO)	Blaine Wt. (grams)	Blaine Time (sec.)	pH
Example 12	480	93.9	0.45	93.7	11.4
Example 13	460	94.6	0.50	173.0	10.4
Example 14	560	96.7	0.35	75.1	10.7
Example 15	420	94.2	0.45	45.7	11.6

Note that the slurry concentration of 0.8 lb/gallon produced the highest brightness and the lowest bulk density.

Example 16 (5XPC 52)

In this example, the same procedures described in example 1 were used, except that the siliceous raw material

52

was changed. Instead of using diatomaceous earth, a source

of 100% pure silica was used (trade name: Min-U-Sil). The

reaction was carried out at a very low CaO - SiO_2 slurry

concentration of 0.2 lb/gallon. The resultant calcium

5   silicate hydrate complex was tested for the same key

pigment properties as in example 1 above. The reaction

conditions and key pigment properties are given in Tables

7a and 7b, respectively.

10   Example 17 (5XPC 55)

In this example, the same procedures described in

example 16 were used (including using the pure silica for a

siliceous source). The only difference here was that the

CaO - SiO_2 slurry concentration was raised to 0.4 lb/gallon,

15   and the temperature was kept at 232 °C. The calcium

silicate hydrate complex formed from this reaction was

tested as in example 16 above. The reaction conditions and

key pigment properties are given in Tables 7a and 7b.

20

53

Table 7a: Reaction conditions for Examples 16 and 17.

Batch #	Mol Ratio (CaO/SiO$_2$)	Conc. (lb/gallon)	Temp. (°C)	Average Pressure (psi)	Reaction Time (hours)
5XPC 52	1.31	.25	245	490	2
5XPC 55	1.31	.4	232	387	2

Table 7b: Pigment Properties Examples 16 and 17

Batch #	G.E. Brightness (%reflectance)	Water Absorption (%)	Air Perm. Blaine Wt. (g)	Air Perm. Blaine time (sec.)
5XPC 52	96.2	920		
5XPC 55	95.1	840		

5

Example 18 Sodium Silicate (5XPC 57)

In this example, all the reaction procedures were kept constant as in example 1. The only difference was the

10   addition of a different siliceous raw material source. Here, 20 parts of the fluxed calcined diatomaceous earth were replaced by liquid sodium silica Na$_2$O - SiO$_2$ ratio of 1:3 (P.Q. "N" product). The overall CaO/SiO$_2$ mol ratio was

kept at 1.31, the concentration of the CaO - SiO_2 slurry was kept at 0.5 lb/gallon, and all the other reaction conditions were kept the same as well. This product was also tested according to the procedures in example 1. The reaction conditions and key pigment properties are given in Tables 8a and 8b, respectively.

Table 8a: Reaction conditions for Examples 18.

Batch #	Mol Ratio (CaO/SiO₂)	Concentration (lb/gallon)	Temperature (°C)	Average Pressure (psi)	Reaction Time (hours)
5XPC 57	1.31	0.5	245	375	2

Table 8b: Pigment Properties Examples 18.

Batch #	GE Brightness (% reflectance)	Water Absorption (%)	Air Permeability Blaine Wt. (g)	Air Permeability Blaine time (sec.)
5XPC 57	97.0	680	0.35	57.5

Note that the most significant difference between this product and the previous example is the high brightness values produced.

5   Example 19 (TiSil Brand CSH vs. PCC)

Application of multi phase calcium silicate hydrate complex comprising predominantly Foshagite, $Ca_4(SiO_3)_3(OH)_2$ and some Xonotlite, $Ca_6Si_6O_{17}(OH)_2$ in paper according to the following process conditions. My novel calcium silicate

10   hydrate complex, referred to as TiSil Brand CSH, was applied in paper handsheets. It was compared to commercial PCC (SMI's Albacar(HO)) and a mixture of PCC and approximately 60 lbs. per ton TiO_2. The results of the testing are given in Table 9a and 9b. The graphs showing

15   the performance of TiSil compared to PCC are given in Figures 6 through 13. Improvement by TiSil over PCC is given in Tables 9c. TiSil Brand CSH gave the following improvement at 20% ash and equal brightness:

20

25

56

Table 9a: Optical property performance of handsheets containing 20% (interpolated) TiSil and 20% (interpolated) PCC.

Pigment	Brightness (ISO)	Opacity (ISO)	Sheet Scattering Coefficient (cm²/g)	Filler Scattering Coefficient (cm²/g)
TiSil	87.2	92.3	858.0	3065.1
PCC	90.0	89.0	716.8	2507.0

Table 9b: Strength property performance of handsheets containing 20% (interpolated) of TiSil and 20% (interpolated) PCC.

Pigment	Stiffness (Gurley Units)	Bulk (cm³/g)	Porosity (sec/100cc air)	Tensile Index (Nm/g)
TiSil	135.3	1.78	47.5	30.0
PCC	113.4	1.58	26.0	29.0

Table 9c: Handsheet results for TiSil vs. PCC

Opacity	+ 2.13%
Scattering Power of sheet	+ 16.2%
Filler Scattering Coefficient	+ 24%
Bulk	+ 9%
Porosity	+ 220%
Stiffness	+ 38.0%
Tensile Strength Index	+ 22.0%

The TiSil brand CSH pigment seemed to improve a combination of properties, which were heretofore unattainable. For example, if sheet bulk was improved, sheet porosity would usually drop. In addition, if sheet bulk was obtained by having a larger particle size, optical properties would be significantly reduced. With my novel

pigment, it is the unique composition and structure of the pigment that allows improvement in key paper properties like higher bulk and lower porosity.

5   Example 20 (TiSil Brand CSH vs. PCC with 60 lb/ton TiO₂)

In this example, the calcium silicate hydrate from example 1 (5XPC12) was compared with a mixture of SMI's Albacar(HO) containing 60lb/ton TiO₂. The results of the paper testing are placed in Tables 10a and 10b. The

10   graphical representations of the data are given in Figures 18 through 25. The improvement TiSil gave over the PCC + TiO₂ mixture (@ 20% ash level and equal brightness) is given in Table 10c.

15   Table 10a: Optical property performance of handsheets containing 20% (interpolated) TiSil and 20% (interpolated) PCC + TiO₂ combination.

Pigment	Brightness (ISO)	Opacity (ISO)	Sheet Scattering Coefficient (cm²/g)	Filler Scattering Coefficient (cm²/g)
TiSil	87.2	92.3	858.0	3065.1
PCC with TiO₂	90.0	89.0	716.8	2507.0

20

25

Table 10b: Strength property performance of handsheets containing 20% (interpolated) of TiSil and 20% (interpolated) PCC + TiO$_2$ combination.

Pigment	Stiffness (Gurley Units)	Bulk (cm^3/g)	Porosity (sec/100cc air)	Tensile Index (Nm/g)
TiSil	135.3	1.78	47.5	30.0
PCC with TiO$_2$	113.4	1.58	26.0	29.0

Table 10c: Handsheet results - TiSil vs. PCC + TiO$_2$ combination

Opacity_____	by 0.5%
Scattering Power of sheet_____	by 3.0%
Filler Scattering Coefficient_____	by 4.0%
Bulk_____	by 8.2%
Porosity_____	by 40.0%
Stiffness_____	by 26.0%
Tensile_____	by 221.0%

Here, TiSil Brand CSH has demonstrated exceptional scattering power for light, an unusual ability to close up the sheet (higher Gurley porosity) and a significant improvement in sheet bulk, stiffness, and tensile index.

Example 21 (TiSil Brand CSH vs. Bulkite - XPC65)

In this example, the pigment of my invention, namely a calcium silicate hydrate complex (Foshagite - Xonotlite complex) was manufactured under the conditions given in Table 11a. The pigment was tested for brightness, water

59

absorption, Blaine, and pH. The results are given in Table
11b. This product was compared as a paper-making pigment
with commercially available calcium silicate, (Trade name
Bulkite). The graphical representation of the results are
given in Figures 26-30. The comparison of the two
pigments, XPC-65 and Bulkite at 20% ash is given in Table
11c. The improvement over Bulkite at 20% ash
(interpolated) is given in Table 11d.

Table 11a: Reaction conditions for Example 21.

Example #	Batch #	Mol Ratio (CaO/SiO$_2$)	Concentration (lb/gallon)	Temperature (°C)	Reaction Time (hours)
Example 21	XPC 65	1.67	0.71	232	2

Table 11b: Pigment properties for Example 21.

Example #	Water Absorption (%)	Brightness (ISO)	Blaine Wt. (grams)	Blaine Time (sec.)	PH
Example 21	420	93.7	0.45	46.2	10.7

60

Table 11c: Optical property performance of handsheets
containing 20% (interpolated) XPC 65 and Bulkite.

Pigment	Opacity (ISO)	Sheet Scattering Coefficient (cm^2/g)	Filler Scat. Coeff. (cm^2/g)	Brightness (ISO)	Porosity (sec/100 cc air)
XPC - 65	90.9	845.4	3109.6	90.0	42.4
Bulkite	84.2	460.9	1273.4	86.4	4.9

5

Table 11d: Summary of TiSil Improvement over Bulkite

Opacity_____	by 7.2%
Scattering Power of sheet_____	by 83.0%
Filler Scattering Coefficient_____	by 144.0%
Brightness_____	by 4.13%
Porosity_____	by 770.0%

10   Once again, this product shows substantially

significant improvement over industry standard pigments.

Example 22 (XPC 117) Application in Newsprint

    In this example, the multi-phase CSH Foshagite -

15 Xonotlite was made by the same procedure as in Example 1,

using the process conditions in Table 12a below.

20

25

Table 12a: Reaction conditions for Example 22.

Example #	Batch #	Mol Ratio (CaO/SiO$_2$)	Concentration (lb/gallon)	Temperature (°C)	Reaction Time (hours)
Example 22	XPC 117	1.67	0.67	224	2

5   The product was tested for brightness, water absorption, Blaine and pH. The results are given in Table 12b.

Table 12b: Pigment properties for Example 22.

Example #	Water Absorption (%)	Brightness (ISO)	Blaine Wt. (grams)	Blaine Time (sec.)	pH
Example 22	470	95.3	0.45	184.7	10.6

10   The calcium silicate hydrate complex of this invention was added to newsprint furnish (20% kraft, 80% TMP). To compare the performance of the product of my invention, handsheets were made using commercially available calcium silicate (Hubersil, JM Huber Co.) and a precipitated

15   calcium carbonate (also by JM Huber Co). The newsprint

62

sheets containing these pigments were tested for the

following:

Sheet bulk, stiffness, porosity, smoothness,

brightness, opacity and several print quality

5 parameters like ink strike through, show through

and overall print through. Sheets were also

tested for the static coefficient of friction.

The actual values, interpolated to 6% ash, are given

10 in Tables 12c and 12d. A comparison of the product of my

invention and Huber's PCC and HuberSil gave the differences

shown in Tables 12e and 12f. The corresponding bar graphs

at 6.0% interpolated ash are given in FIGS. 31 through 39.

15 Table 12c: Optical property performance of handsheets
containing 6% (interpolated) TiSil, HuberSil, and Huber
Carbonate.

Pigment	Normalized Opacity (ISO)	Ink Penetration	Show Through	Print Through
TiSil	86.29	1.46	4.67	6.13
HuberSil	85.33	1.60	5.14	6.74
Huber Carbonate	86.75	2.46	4.79	7.24

20

25

63

Table 12d: Strength property performance of handsheets containing 6% (interpolated) TiSil, HuberSil, and Huber Carbonate.

Pigment	Porosity (sec/100 cc air)	Tensile Index (Nm/g)	Stiffness (Gurley Units)	Static Coeff. of Friction	Sheet Smoothness (Sheffield Units)
TiSil	15.40	25.57	22.08	0.90	159.76
HuberSil	11.93	21.95	24.31	0.90	176.02
Huber Carbonate	11.36	25.32	18.06	0.86	164.06

Table 12e: Summary of Improvement over Huber Carbonate

Opacity	-0.53%
Ink Penetration	40% less (better)
Show through	2.0% less (better)
Overall print through	15.0% less (better)
Porosity	+ 35.0% (better)
Tensile	even
Stiffness	+ 22% (better)
Static coefficient of friction	+ 5.0% (better)

A comparison of my new multi-phase CSH products with

Huber's calcium silicate gave the following

Table 12f: Summary of Improvement over HuberSil

Opacity	+1.1 points
Ink Penetration	9.0% less (better)
Show through	9.0% less (better)
Overall print through	9.0% less (better)
Porosity	+ 29.0% (better)
Tensile	+16.0% (better)
Shefield smoothness	10.0% less (better)

Once again, my multi-phase CSH product gives better paper and printing properties than currently available commercial calcium carbonate and commercial calcium silicate fillers.

5   During testing of my novel multi-phase calcium silicate hydrate products, conventional industry quality control standards were observed. Brightness was tested by using a GE/TAPPI Brightness Meter, Model S-4. Where applicable, the pH was tested with a pH meter utilizing

10   TAPPI method T-667. Pulp beating was performed using a Valley Beater according to TAPPI Method T-200. Handsheets were produced using a British Handsheet Mold according to TAPPI Method T-205. Handsheet testing was for tensile strength used a one inch strip and otherwise was conducted

15   according to TAPPI method T-220. Where applicable, freeness was tested utilizing a Canadian Standard Freeness tester according to TAPPI standard T-227. Ashing tests were conducted at 500 °C according to TAPPI Method T-211. Air permeability testing was conducted by Blaine, ASTM

20   Method C204. Available lime was measured according to ASTM Method C25. For fine paper testing, a standard pulp slurry was made up of 75% hardwood and 25% softwood. Both pulp sources were beaten separately, in a Valley Beater, to a

specific Canadian Standard Freeness of 450 ± 10 in accordance with TAPPI test methods T-200 and T-227. for newsprint testing, a standard newsprint pulp slurry was made up of 20% softwood kraft fibers, and 80% thermo-

5   mechanical pulp. Both pulp sources were received with Canadian Standard Freeness values of 180 csf ±25. This freeness value was deemed sufficient and no further beating was performed on the pulp. For the disintegration of the stock pulp solutions, hot water was added to help relax the

10   pulp fibers and prevent fiber clumps in the final sheet. Handsheets were formed from the above prepared stock, on a 6" British handsheet mold, in accordance with TAPPI test method T-205. However, since the goal of producing these handsheets was to test filler performance, some filler was

15   incorporated into the handsheets at various replacement levels (usually 15%, 20%, and 25%). In order to achieve comparability between different replacement levels, a constant basis weight was achieved via a reduction in fiber content. Thus, a 25% filled sheet contained only 75% of

20   the fiber that the unfilled sheet has. Also, a retention aid was utilized to hold the filler in the sheet until the sheet had dried completely. All other handsheet formation components were kept consistent with TAPPI test method T-

205. Handsheets utilizing titanium dioxide in fine paper were similarly formed, except that they required double the amount of retention aid as required by the other fillers. In addition, when TiO_2 was added in conjunction with another

5   filler, it was necessary to first add TiO_2, then add one dose of retention aid, and then add the filler and a second dose of retention aid. Handsheets formed for newsprint testing were prepared in a similar method to the fine paper handsheets. However, different filler loading levels were

10   utilized. and the newsprint sheets were usually loaded at 3%, 6%, and 9% filler. The handsheets were tested in accordance with TAPPI test method T-220, except that a 25.4mm sample was used and the tensile index calculations were recalculated accordingly. Handsheets were ashed in

15   accordance with TAPPI test method T-211.

In summary, the unique crystalline microfibres produced as a product of the reactions described herein exist, in one unique product, as bundles sized from about 10 to about 40 microns, typically occurring as haystacks or

20   balls. Preferably, individual fibers are about 0.2 microns in the largest cross-sectional dimension, with lengths of up to 4 or 5 microns, so as to have a relatively large L/D ratio.

Importantly, the crystalline microfibers as just described have advantageous properties when utilized as a paper filler, particularly in uncoated groundwood, and in coated groundwood, in uncoated fine paper, and in coated

5   fine paper. The aforementioned adsorptive properties help to adsorb printing ink in the papers. Also, it helps the paper sheet itself to absorb fines, so that it improves overall sheet retention during the papermaking process. Overall, final paper products exhibit improved porosity,

10   improved smoothness, improved bulk, and improved stiffness. Also, brightness and opacity are maintained or improved. Moreover, the printability of the final product is significantly improved, due to the improved ink adsorption.

It is to be appreciated that my unique, light, fluffy

15   adsorptive calcium silicate hydrate products, and the method of producing the same, and the paper products produced using such products, each represent an appreciable improvement in the paper production arts. Although only a few exemplary embodiments of this invention have been

20   described in detail, those skilled in the art may find that the processes described herein, and the products produced thereby, may be modified from those embodiments provided

herein, without materially departing from the novel

teachings and advantages provided.

It will thus bee seen that the objects set forth

above, including those made apparent from the preceding

5   description, are efficiently attained. Since certain

changes may be made in carrying out production of the CSH

products, and the unique paper products produce therewith,

it is to be understood that my invention may be embodied in

other specific forms without departing from the spirit or

10 essential characteristics thereof. Many other embodiments

are also feasible to attain advantageous results utilizing

the principles disclosed herein. Therefor, it will be

understood that the foregoing description of representative

embodiments of the invention have been presented only for

15 purposes of illustration and for providing an understanding

of the invention, and are not intended to be exhaustive or

restrictive, or to limit the invention to the precise

embodiments disclosed. The intention is to cover all

modifications, equivalents, and alternatives falling with

20 .the scope and spirit of the invention, as expressed herein

above and in the appended claims. As such, the claims are

intended to cover the products, processes, methods, and

equivalent processes and methods. The scope of the

invention, as described herein, is thus intended to

included variations from the embodiments provided which are

nevertheless described by the broad meaning and range

properly afforded to the language herein, and as explained

5   by and in light of the terms included herein, or by the

legal equivalents thereof.